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#### COMPLETE SPECIFICATION.

#### Phthalocyanine Heterocyclicsulfonamides.

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, of 230 Park Avenue, New York, County and State of New York, United States of America, (Assignees of Arthur L. Fox, a citizen of the United States of America, of 118 Parker Avenue, Easton, County of Northampton, Commonwealth of Pennsylvania, United States of America), do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of new phthalocyanine sulfonamides.

The term phthalocyanine is used herein in the generic sense to define tetraazaporphins in which each of the four pyrrole nuclei is fused to an aromatic nucleus, e.g., phenyl, diphenyl, naphthyl, anthranyl, of which phthalocyanine itself (tetraazaporphin) is a well-known example. The phthalocyanine molecule may be metal free or contain a metal in complex combination, for example, copper, cobalt, nickel, iron or aluminium.

Specification No. 520199 describes and claims the manufacture of phthalocyanine sulfonamides by causing ammonia or amines to react upon phthalocyanine sulfonylchlorides. Among the sulfonamides therein described are those derived from the secondary heterocyclic amine, perhydrocarbazole.

The present invention consists in a process for the manufacture of phthalocyanine secondary heterocyclic sulfonamides which comprises condensing a phthalocyanine sulfonylchloride with 2-, 3- or 4-aminopyridine.

The preparation of the new sulfonamides from the phthalocyanine sulfonylchloride and the heterocyclic amine may be carried out at elevated temperature, but preferably is conducted at room or even lower temperatures. The reactions may be carried

out in aqueous solution or suspension, in the presence of an organic solvent such as 50 alcohol, acetone, nitrobenzene, as may be found most suitable, or in some instances in the complete absence of a diluent.

The new compounds are phthalocyanines containing attached to the arylene nuclei at 55 least one sulfonamide group which is substituted by the heterocyclic residue of the starting amine. The number of these sulfonamide groups may vary from one to four or more depending on the number of 60 sulfonylchloride groups present on the arylene nuclei of the starting phthalocyanine. In some instances the products may also contain attached to the arylene nuclei one or more sulfonic acid groups, 65 either free or as the amine salt, not all the sulfonylchloride groups being converted in the reaction to sulfonamide groups, or other substituents such as halogen atoms, e.g., chlorine, or amino or carboxy groups. 70

Compared with the corresponding tertiary sulfonamides derived from the secondary amine, perhydrocarbazole, the new secondary sulfonamides derived from 2-, 3- or 4-aminopyridine are compounds 75 possessed of a much greater solubility in water and in dilute caustic alkali.

The new phthalocyanine colors are of a brilliant blue to greenish-blue shade and are capable of dyeing various textile fibers such 80 as cotton, wool and silk. Where the molecule additionally contains sulfonic acid groups, either free or in the form of an amine salt, they are capable of being converted into color lakes with, for example, 85 calcium or barium salts. Certain of these new sulfonamides are eminently suited for the coloring of writing inks, for example, the sulfonamide from the tetrasulfonylchloride of copper phthalocyanine, on the 90 one hand, and 2-aminopyridine, on the other, the dye-stuffs being employed for this purpose in the form of their soluble salts, particularly, sodium, potassium, ammonium and lithium. A further characteristic of these ink colors is their stability

in dilute aqueous caustic alkali solutions over relatively long periods of time, a property rendering them particularly suited for coloring of writing inks rendered quick drying by a small content of caustic alkali, e.g., caustic soda. As colors in such quick-drying inks, they are quite resistant to bleaching by water and characterized by their light fastness and outstanding brightness.

The starting phthalocyanine sulfonylchlorides employed in the preparation of the phthalocyanine sulfonamides may be obtained by reacting chlorosulfonic acid with the corresponding phthalocyanines at an elevated temperature as described in Specification No. 515,637. They may also be made from the corresponding phthalocyanine sulfonic acids or their salts by treatment with phosphorus pentachloride.

The invention is further illustrated by the following specific example to which, however, it is not to be limited. Parts are by weight unless otherwise noted.

## EXAMPLE.

Ten parts of copper phthalocyanine tetrasulfonylchloride is slowly stirred into a solution of 10 parts of 2-aminopyridine in 100 parts of nitrobenzene and the resulting mixture stirred for 10-12 hours at room temperature. The nitrobenzene is then removed from the reaction mixture by means of a steam distillation and the resulting solution evaporated to a thick syrupy residue. Upon cooling, the residue

is poured into 100 volumes of 10% hydrochloric acid and the precipitate filtered and dried. A bright blue dyestuff is obtained in approximately quantitative yield which is quite soluble in dilute aqueous caustic alkali.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is

1. Process for the manufacture of phthalocyanine sulfonamides which comprises condensing a phthalocyanine sulfonylchloride with 2-, 3- or 4- aminopyridine.

2. Process as claimed in Claim 1, wherein the phthalocyanine compound is a metal phthalocyanine polysulfonylchloride.

3. Process as claimed in claim 2, wherein the metal of the phthalocyanine polysulfonylchloride is copper.

4. Process for the manufacture of phthalocyanine sulfonamides which comprises condensing copper phthalocyanine tetrasulfonylchloride with 2-, 3- or 4- aminopyridine.

5. Phthalocyanine sulfonamides whenever prepared by the process as claimed in any of the preceding claims.

Dated this 2nd day of July, 1946.

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